

METHOD AND APPARATUS FOR CONTROLLING CONCENTRATION OF ELECTROLYTIC SOLUTION

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates to a method and an apparatus for controlling a concentration of electrolytic solution which is used for electrolytic treatment of a metallic material.

2. Description Related to the Prior Art

10 In general, an aluminum substrate is used as a substrate of a presensitized plate (hereinafter PS plate) for offset printing. When the printing is made on the PS plate, the hydrophilic property and the ink-philic property (or lipophilic property) are controlled. Accordingly, in order to print images 15 of high quality, a surface of the aluminum substrate is roughened to make the surface uniform. As the method of roughening the surface of the aluminum substrate, there is an electrolytic treatment. In a production line of PS plate is used an electrolytic treatment apparatus in which the aluminum 20 substrate is drenched in the electrolytic solution and generates an electrolytic current is supplied between electrodes in the electrolytic solution to make the electrolytic treatment.

Generally, the electrolytic solution used in the 25 electrolytic solution is a solution in which many components are dissolved, and contains metallic ions, and one of hydrochloric acid, nitric acid and sulfuric acid or a mixture of at least two of these acids. Accordingly, in order to keep the situation of the reaction of electrolytic treatment uniform, 30 the concentration of each component in the electrolytic solution is measured in performance of the electrolytic

treatment, and the data obtained in the measurement is sent to a controller for controlling the concentration of the each component in the electrolytic solution. As a known method of measuring the concentration of each component, there is a 5 neutralization titration. However, it takes a long time to perform the neutralization titration, and metal hydroxides precipitate in the titration pollutes a cell and a pipe, and are hardly removed from them.

Japanese Patent Laid-Open Publication No.4-19559 solves 10 these problems in the method of the neutralization titration. In the method of this publication, a mixture solution whose concentration ratio is known is prepared. Then several physical quantities (temperature, electric conductivity, propagation speed of ultrasonic wave) of the mixture solution are measured. 15 On the basis of the result of the measurement, a data map of each component that illustrates a relation of the physical quantities to the concentration is made. Thereafter, the measurement of plural physical quantities of the electrolytic solution is made, and in reference with the data map, the 20 concentration of each component is obtained from the measured physical quantities.

Further, in Japanese Patent Laid-Open Publication No.2001-121837, a data table is previously prepared. Then, at least two physical quantities are measured, and the 25 concentration of each component in the electrolytic solution containing the metallic ions is obtained from the obtained value of the physical quantities, in reference with the data table. Thereafter, on the basis of the obtained values and the like in the measurement, the concentration of the electrolytic solution is controlled in a predetermined range in the method 30 of a feed-back method, a feed-forward method, or a combination

of these methods, so as to keep the treatment conditions uniform.

When the concentration control is performed in single one or combination of the feed-back and feed-forward methods, a PID 5 control is generally utilized. In the PID control are combined a proportional control (P), an integral control (I) and a differential control (D). However, a device of the PID control is expensive, which causes to make the cost for equipment higher. Further, in the device of the PID control, many extra articles 10 for preservation of the device and a person responsible for the preservation, who has specialized knowledge, are necessary. Further, the concentration control can be made only with use of a programmable controller. In this case, however, a complicated calculation of amount of components to be supplied 15 for the concentration control must be made. Further, a programmable controller of high speed and high function. Accordingly, the device therefor is so expensive as the device for the PID control, and high knowledge and skills are necessary for preservation of the device.

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SUMMARY OF THE INVENTION

An object of the present invention is to provide a method and an apparatus for controlling a concentration of an electrolytic solution easily.

25 In order to achieve the object and the other object, in a method for controlling a concentration of an electrolytic solution used for an electrolytic treatment of the metallic material, a measured acid concentration of acid in the electrolytic solution is measured. In the electrolytic treatment, part of the metallic material is ionized to generate 30 a salt, and a measured salt concentration is measured. Then at

least one of a predetermined amount of a diluting liquid and a fresh acid is added in accordance with the measured acid concentration, the measured salt concentration and total current of the electrolytic current used for the electrolytic treatment.

An apparatus of the present invention for controlling a concentration of an electrolytic solution used for an electrolytic treatment of the metallic material includes an acid concentration meter for measuring a concentration of acid contained in the electrolytic solution, and a salt concentration meter for measuring a concentration of salt which is generated by ionizing part of the metallic material in the electrolytic treatment. A current meter measures a current value of current supplied during electrolytic treatment. The apparatus of the present invention further includes an acid concentration control means for controlling the concentration of the acid, and a salt concentration control means for controlling the concentration of the salt. The acid concentration controlling means adds a predetermined amount of a fresh acid to the electrolytic solution on the basis of a measured value and a preset value of the concentration of the acid. The salt concentration control means calculates a cycle of the concentration control of the electrolytic solution, and add a diluting solution to the electrolytic solution at every cycle.

According to the method and the apparatus of the present invention, the concentration control of the electrolytic solution can be made with used of a cheap programmable controller instead of the expensive controller such as the PID controller. Further, an electrolytic treatment apparatus can have a simple structure. Thus a cost for producing and

maintaining the equipment can be decreased.

BRIEF DESCRIPTION OF THE DRAWINGS

The above objects and advantages of the present invention
5 will become easily understood by one of ordinary skill in the art when the following detailed description would be read in connection with the accompanying drawings.

Figure 1 is a schematic diagram of production line of a PS plate;

10 Figure 2 is a schematic diagram illustrating an electrolytic treatment apparatus to which a method of controlling a concentration of electrolytic solution is applied;

15 Figure 3 is a block diagram illustrating a concentration control of the electrolytic treatment apparatus in FIG.2.

PREFERRED EMBODIMENTS OF THE INVENTION

In FIG.1, in a PS plate production line 10, a continuous
20 and thin aluminum web 11 is used as a substrate of a PS plate. The aluminum web 11 is wound in an aluminum roll 12, which is set to the PS plate production line 10. In downstream of the aluminum roll 12, an etching apparatus 13, an electrolytic treatment apparatus 14, an oxidization apparatus 15, a first
25 coater 16, a second coater 17, a cutter 18, and an stacker 19 are provided on a transporting path of the aluminum web 11.

Several surface treatments for the aluminum web 11 unwound from the aluminum roll 12 are made in the etching apparatus 13, the electrolytic treatment apparatus 14 and the
30 oxidization apparatus 15. Then the first and second coaters 16, 17 apply solutions of photosensitive compounds onto the surface

of the aluminum web 11, and the solutions are dried to form a photosensitive layer. Thereafter, the aluminum web 11 is cut by the cutter 18 into PS plates 11a having predetermined size, and the PS plate 11a are accumulates as semiproducts by the 5 stacker 19. The method and the apparatus for controlling the concentration of the electrolytic solution of the present invention can be mainly applied to the electrolytic treatment apparatus 14.

As shown in FIG.2, in the electrolytic treatment 10 apparatus 14, the aluminum web 11 is drenched to an electrolytic solution 20 which mainly contents is hydrochloric acid. Simultaneously, a current is generated to roughen uniformly the surface of the aluminum web 11. Note that, in the apparatus for electrolytic treatment, there are several types, for example 15 a flat type and a radial type. The electrolytic treatment apparatus 14 is provided with plural path rollers 25 for transporting the aluminum web 11 in a transporting direction, and an electrolytic treatment bath 26 is provided on the transporting path of the aluminum web 11 supported by the path 20 rollers 25. Note that the path roller 25 is formed of, for example, chloroprene rubber, in consideration with protection of the surface of the aluminum web 11 and the resistance to hydrochloric acid.

The electrolytic treatment bath 26 is filled with the 25 electrolytic solution 20, and the path rollers 25 are disposed so as to drench the aluminum web 11 into the electrolytic solution 20. The path rollers 25 contact the aluminum web 11 with a predetermined contact pressure to guide the aluminum web 11, and tenses the aluminum web 11 in the transporting direction 30 (or a lengthwise direction of the aluminum web 11). Further, the electrolytic treatment bath 26 is provided with a

temperature controller (not shown), which reduces the fluctuation of the temperature of the electrolytic solution 20 to keep the predetermined condition for the reaction of electrolytic treatment.

5 In the electrolytic solution 20 in the electrolytic treatment bath 26, two electrodes 28 having plate shapes are arranged in the transporting direction so as to confront to an upper surface of the drenched aluminum web 11. Note that the number of the electrodes is not determined. However, the current density is usually different between sides and center of each electrode. However, it is necessary that the electric current density in the electrolytic solution 20 is uniform in the transport direction of the aluminum web 11. Accordingly, it is preferable to provide the plurality of the electrodes along the 10 transporting path of the aluminum web 11. Further, the electrodes 28 is longer than the aluminum web 11 in widthwise direction such that the current may be generated uniform in the widthwise direction. The electrodes 28 are connected through bus bars 29 to a power source section 30.

20 In this embodiment, alternating current is used as the electric current generated by the power source section 30 for electrolytic treatment. However, the alternate current and the direct current that are simultaneously generated may be superposed to use as the current between the electrodes. The 25 shape of the alternative current is not especially restricted, and the alternative current may be a sinusoidal current, a rectangular current, a triangular wave current and the like. Further, a cycle of the alternative current, a DUTY ratio and the like are set to adequate values, so as to control a reaction period for reaction of the aluminum web as anode and that for reaction of the aluminum web as cathode. Thus the roughening 30

treatment of the surface of the aluminum web 11 is uniformly made.

The electrolytic treatment apparatus 14 is used in combination with a concentration control device constructed of 5 a solution tank 32 and a controller section 38. The solution tank 32 is positioned below the electrolytic treatment bath 26, and they are combined through a feed-back pipe 33, an overflow pipe 34, and a solution supplying pipe 35. In the solution tank 32, the measurement and the control of the concentration of 10 components in the electrolytic solution 20 are made. In the controller section 38 there are an acid concentration controller 39 and a salt concentration controller 40, which are used for controlling the concentration of the electrolytic solution 20 in the solution tank 32, as described below. An 15 upper end of the feed-back pipe 33 is connected to a bottom of the electrolytic treatment bath 26 to form an opening through which the electrolytic solution 20 is fed back toward the solution tank 32. In a middle of the feed back pipe 33, a valve 36 is provided. When the electrolytic treatment is made, the 20 valve 36 is controlled to open. Accordingly, the electrolytic solution 20 starts flowing through the feed-back pipe 33 to the solution tank 32 at a nearly constant flow rate.

An upper end of the overflow pipe 34 is connected to a side wall of the electrolytic treatment bath 26, and a lower 25 end is inserted into the electrolytic solution 20 in the solution tank 32. When the surface of the electrolytic solution 20 in the electrolytic solution cell 26 is higher than a lower edge of an opening of the overflow pipe 34 on the side wall of the electrolytic treatment bath 26, then the electrolytic solution 20 starts flowing from the electrolytic solution cell 26 through the overflow pipe 34 to the solution tank 32.

Therefore, the level of the electrolytic solution 20 does not higher than the predetermined upper limit level.

A lower end of the solution supplying pipe 35 is connected to a lower side of a side wall of the solution tank 32, and an 5 upper end is positioned inside the electrolytic treatment bath 26 and above the electrolytic solution 20. Further, the solution supplying pipe 35 is provided with a pump 37. When the pump 37 is driven, the electrolytic solution 20 is fed out from the solution tank 32 and supplied into the electrolytic treatment 10 bath 26. The electrolytic solution 20 is circularly fed between the electrolytic treatment bath 26 and the solution tank 32. Accordingly, when the concentration of components in the electrolytic solution 20 is controlled in the solution tank 32, the concentration of the electrolytic solution 20 in the 15 electrolytic treatment bath 26 is kept in a predetermined range.

The control of the concentration of the electrolytic solution 20 in the solution tank 32 is made in the controller section 38. The controller section 38 controls the concentrations of the hydrochloric acid (as the main content) 20 and the aluminum chloride in the electrolytic solution 20 in respectively predetermined ranges. The aluminum chloride is a metallic salt which is generated by the ionization of the aluminum atoms on the surface of the aluminum web 11 in the electrolytic treatment, and is dissolved to the electrolytic 25 solution 20. When the concentration of the aluminum chloride (hereinafter salt concentration) in the electrolytic solution 20 becomes lower, the reaction speed of the reaction in the electrolytic treatment becomes higher, and then the salt concentration becomes higher, the reaction speed becomes lower. 30 In the present invention, not only the hydrochloric acid but also the concentration of the aluminum chloride are controlled

such that the electrolytic treatment to the transported metallic substrate is uniformly made. In this embodiment, the controller section 38 has the acid concentration controller 39 and the salt concentration controller 40 so as to control the 5 respective concentrations of the hydrochloric acid and the aluminum chloride in the electrolytic solution 20.

In order to control the concentration of the hydrochloric acid (hereinafter acid concentration) in the electrolytic solution 20, the hydrochloric acid is fed into the solution tank 10 32 in actuation of the acid concentration controller 39. In order to control the salt concentration in the electrolytic solution 20, the water (preferably, pure water) is fed into the solution tank 32 in actuation of the salt concentration controller 40 and added to the electrolytic solution 20 in the 15 solution tank 32. Further, each of the acid and salt concentration controllers 39, 40 is a programmable controller which is constructed of a CPU, a RAM and the like for operating input data.

As shown in FIG.3, the acid concentration controller 39 20 is connected to an acid concentration meter 41 and an acid feeding section 42. The acid concentration meter 41 measures the acid concentration of the electrolytic solution 20 in the solution tank 32, for example once at 10 seconds, and sends the acid concentration controller 39 an acid concentration data 25 obtained in the measurement. For example, as the acid concentration meter 41, a densitometer, a titlator or the like is used.

An acid concentration data of the measured acid concentration of hydrochloric acid is input into the acid 30 concentration controller 39, and then sent to a difference discriminator 43. The difference discriminator 43 calculates

the difference the measured acid concentration and the predetermined acid concentration of the electrolytic solution 20, on the basis of the acid concentration data. When the difference is larger than a predetermined value, then the
5 difference discriminator 43 discriminates that it is necessary to add the hydrochloric acid to the electrolytic solution 20 in the solution tank 32. In this case, the acid concentration controller 39 sends an acid feed signal to the acid feeding section 42.

10 When the acid feed signal is input into the acid feeding section 42, the acid feeding section 42 starts feeding the undiluted hydrochloric acid to the solution tank 32. The acid feeding section 42 is constructed of an acid feed pipe 44, a hydrochloric acid tank (not shown), a solenoid valve 45, an
15 automatic valve 46, a acid feed pump 47 and the like. An end of the acid feed pipe 44 is connected to the hydrochloric acid tank, and another end is connected to the solution tank 32 on the surface of the electrolytic solution 20. Further, the automatic valve 46 and the acid feed pump 47 are positioned on
20 the acid feed pipe 44. The automatic valve 46 is opened and closed in accordance with the operation of the solenoid valve 45. When receiving the acid feed signal, the automatic valve 46 are opened. When receiving the acid feed signal, the acid feed pump 47 is driven to feed the undiluted hydrochloric acid from the
25 hydrochloric acid tank to the solution tank 32. Thus the undiluted hydrochloric acid is added to the electrolytic solution 20 in the solution tank 32.

As shown in FIG.2, the salt concentration controller 40 is connected to a salt concentration meter 48, the power source
30 section 30, and a water feeding section 49. The salt concentration meter 48, as same as the acid concentration meter

41, measures the salt concentration of aluminum chloride in the electrolytic solution 20 contained in the solution tank 32, and sent the salt concentration controller 40 a salt concentration data of the measured salt concentration of aluminum chloride.

5 For example, as the salt concentration meter 48, there are a AlCl₃ densitometer, a titlator or the like for calculating the concentration of aluminum hydrochloride from electric conductivity or other physical quantities that are measured with use of ultrasonic wave and the like.

10 Further, the power source section 30 sends the salt concentration controller 40 a current value data of a total current supplied during the electrolytic treatment. The total current value is total of current values of the two electrodes since the currents are supplied to the two electrodes 28. A 15 quantity of aluminum dissolving to the electrolytic solution in a unit time varies in accordance with the current value of the total current. Note that the amount of metal (aluminum in this embodiment) dissolved to the electrolytic solution in unit time is determined as electrolytic treatment quantity.

20 As shown in FIG.3, the salt concentration data and a total current data input into the salt concentration controller 40 is sent to a water feed cycle operating unit 50 in the salt concentration controller 40. The water feed cycle operating unit 50 calculates a cycle of supplying water (described below) 25 on the basis of the input salt concentration data and the input total current data. The salt concentration controller 40 sends a water feed signal to the water feeding section 49 at every cycle calculated by the water feed cycle operating unit 50. Further, the salt concentration controller 40 is provided with 30 a water feed period controller 51 which controls a period for feeding the predetermined amount of the water in each water feed

period.

The water feeding section 49 feeds the water into the solution tank 32 to add to the electrolytic solution 20 when the water feed signal is input. The water feeding section 49 5 substantially has the same structure as the acid feeding section 42, and constructed of an water feed pipe 52, a water tank (not shown), a solenoid valve 53, an automatic valve 54, a water feed pump 55 and the like.

The acid concentration data generated in the acid 10 concentration meter 41 is input through an AI (Analog Input) into the acid concentration controller 39. A measured value PV_b of the acid concentration of the hydrochloric acid is displayed on a panel (not shown) provided for the controller section 38 or a display of a personal computer (not shown) connected to 15 the controller section 38.

A correction value is added to the measured value PV_b in order to correct the error of the measuring device or the measuring method. After the correction, the corrected measured value PV_b is displayed on a display panel. In this case, when 20 the measured value PV_b is not in the predetermined range, a warning notice is displayed. Simultaneously, the measured value PV_b after the correction is sent to the difference discriminator 43, so as to perform an operation for and discrimination of controlling the acid concentration of the hydrochloric acid. 25 And a setting value SV_b of acid concentration and a preset value e are input through a keyboard into the difference discriminator 43. When the difference from the measured value PV_b to the setting value SV_b is larger than the preset value e , namely $SV_b - PV_b > e$, the acid feed signal is generated and sent through 30 a DO (DigitalOut) to the solenoid valve 45 and the acid feed pump 47. Thereby, an image representing the feed of the

hydrochloric acid is displayed.

The salt concentration data sent from the salt concentration meter 48 is input into the salt concentration controller 40. The correction value is added to the measured value PV_a of the salt concentration of the aluminum chloride, and then the measured value PV_a is sent to the water feed cycle operating unit 50. Further, a total current value I of the current supplied during the electrolytic treatment and the preset value SV_a of the salt concentration are input.

In the water feed cycle operating unit 50, the inverse of the current value I is multiplied by an optional coefficient A, and further added to an optional coefficient B. Thus the standard feed water cycle T_o is obtained in the following formula:

$$T_o = A/I + B$$

The standard feed water cycle T_o is determined as a cycle for water supplying depending on electrolytic treatment quantity. In the actual electrolytic treatment apparatus, as there are many elements of errors, the correction must be made to the standard feed water cycle T_o . Accordingly, the water feed cycle operating unit 50 calculate a feed water cycle in the following formula wherein C, D are optical coefficients:

$$T = T_o \times (1 + C \times (PV_a - SV_a)) + D$$

The optional coefficients A-D varies according to material and transporting speed of the aluminum web 11, concentration and temperature of the electrolytic solution 20, largeness and number of the electrodes, and the like. Accordingly, it is necessary to set a predetermined value according to the variation of the aluminum material and the electrolytic treatment apparatus. On the basis of the calculated feed water cycle T , the water feed cycle operating unit 50 sends the water

feed signal through the water feed period controller 51 to the solenoid valve 53 and the water feed pump 55. Note that since the feed water period for feeding water is previously input into the water feed period controller 51, the water feed signal is generated for the feed water period for feeding water. Further, an image showing the feeding water is displayed.

As described above, as a simple operation formula is used for controlling the concentrations of hydrochloric acid and aluminum hydrochloride in the electrolytic solution 20. Accordingly, the control of the concentration can be made with use of a cheap programmable controller even though the expensive control device, such as PID controller, is not used.

Effects of the above embodiment will be explained, and the explanation start with the control process of the acid concentration of the hydrochloric acid. The measured value PV_b of the acid concentration in the electrolytic solution 20 is measured by the acid concentration meter 41, and sent to the difference discriminator 43 in which the setting value SV_b of the acid concentration and the preset value e are previously input.

In the condition of $SV_b - PV_b > e$, the difference discriminator 43 outputs the acid feed signal to the solenoid valve 45 and the acid feed pump 47. And the drive of the acid feed pump 47 starts, and the hydrochloric acid is fed to the electrolytic solution 20 in the solution tank 32. Thus the acid concentration of the electrolytic solution 20 becomes higher. When the measured value PV_b of the acid concentration satisfies the condition of $SV_b - PV_b \leq e$, the difference discriminator 43 stops sending the acid feed signal. Corresponding to the stop of the acid feed signal, the solenoid valve 45 is operated to close the automatic valve 46, and the drive of the acid feed

pump 47 stops. The acid concentration meter 41 continuously measures the acid concentration, and in the condition $SV_b - PV_b > e$, the acid concentration of the hydrochloric acid in the electrolytic solution 20 is controlled by repeating the above processes.

Then, the processes of controlling the salt concentration of the aluminum chloride will be explained. The data of the total current value I of the current supplied during the electrolytic treatment and that of the measured value PV_a of the salt concentration which is measured by the salt concentration meter 48 are sent to the water feed cycle operating unit 50 in which the preset value SV_a is input. Then the feed water cycle T is calculated.

At every feed water cycle T , the water feed signal is output to the solenoid valve 53 and the water feed pump 55. When the water feed signal is output, the solenoid valve 53 opens the automatic valve 54. Simultaneously, the drive of the water feed pump 55 starts to feed the water in the water tank to the solution tank 32 to add to the electrolytic solution 20. The feed water period is controlled by the water feed period controller 51. When the feed water period passes, the solenoid valve 53 closes the automatic valve 54, and the feed water pump stops. The salt concentration in the electrolytic solution 20 is controlled by repeating the above processes at every feed water cycle T .

In this embodiment of the electrolytic treatment apparatus for the production line of PS plate, an aluminum material is dipped into the electrolytic solution whose main content is hydrochloric acid, and the electrolytic treatment of the aluminum material is made. However, the present invention can be applied to treatment apparatus of a surface

of several metallic materials with electrolytic reaction in the electrolytic solution, for example, to a oxidization apparatus for the production line of PS plate, other several treatment apparatus, and the like.

- 5 Various changes and modifications are possible in the present invention and may be understood to be within the present invention.

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